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The dissociation of liquid silica at high pressure and temperature

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Liquid silica at high pressure and temperature is shown to undergo significant structural modifications and profound changes in its electronic properties. Temperature measurements on shock waves in silica at 70-1000 GPa indicate that the specific heat of liquid SiO₂ rises well above the Dulong-Petit limit, exhibiting a broad peak with temperature that is attributable to the growing structural disorder caused by bond-breaking in the melt. The simultaneous sharp rise in optical reflectivity of liquid SiO₂ indicates that dissociation causes the electrical and therefore thermal conductivities of silica to attain metallic-like values of $1\text{-}5 \times 10^5$ S/m and 24-600 W/m.K respectively.

Silica (SiO₂) in its various high-pressure phases is of evident importance in the earth's interior and is a prototype material for studying condensed matter physics, materials science, and chemistry under extreme conditions [1]. A major gap in understanding however concerns the behavior of silica in its liquid phase at combined high pressure and temperature. Liquid silicates in this state dominated the earth during late-stage accretion when giant impacts caused complete melting of the planet [2], thereby creating the conditions under which final differentiation of the core and mantle occurred [3]. Present-day remnants of such large magma oceans may still exist as partially-melted zones at the core-mantle boundary [4] and could play an important role in magnetic-field and heat transport between the core and mantle.

The high melting temperature of silica presents a serious challenge to experiments on the liquid at elevated pressures and historically data has been inferred either from glasses at high pressure, or liquids at low pressure. In particular, increasing pressure has been shown to cause a gradual change of the open-network tetrahedral structure in silicate glasses to a closely-packed, six-fold coordinated system [5, 6]. In comparison, increasing temperature causes a continuous reduction in the average size of structural units, or depolymerization, in the liquid that results in elevated specific heat capacities and orders-of-magnitude changes in viscosity [7, 8]. As with all planetary interior processes however, it is the combined effect of high pressure and temperature that is the most relevant yet the most difficult to study. Here we use shock waves to simultaneously compress and heat two polymorphs of silica well into the dense liquid regime. Achieving a broad range of temperatures in the liquid allows us to demonstrate how the features observed near melting - a high specific heat, and a sudden rise in electronic conductivity - represent the onset of an extended process of liquid structural change that continues up to several times the melting temperature.

Using 100 to 500 J of ultraviolet laser light from the OMEGA facility [9] laser-driven shock waves were launched in 500 μm thick samples of fused silica ($\rho_0 =$

2.2 g/cm³) or z-cut α -quartz ($\rho_0 = 2.65$ g/cm³) (a detailed target description has been given previously [13]). This energy was delivered in 1 nanosecond (ns) over a uniformly-irradiated 600 μm spot, generating a planar, attenuating shock wave that provided access to a continuous range of shocked states on a single shot. Two shock diagnostics were used: (1) A Velocity Interferometer System for Any Reflector (VISAR) [10], which measured the shock velocity and reflectivity at a wavelength of 532 nm, and (2) A streaked optical pyrometer (SOP), an absolutely calibrated, space and time-resolved pyrometer used to image the thermal emission between 600 - 700 nm (see Ref. [11] for a description of a similar setup). To determine temperature from the measured emission, grey-body emission was assumed where the emissivity was given by $1-R$ with R given by the measured optical reflectivity. The assumption of grey-body emission at 600-700 nm was verified previously at low pressure by measuring emission at multiple wavelengths [12]. Both the VISAR and SOP provide continuous measurements of the shock velocity, temperature, and reflectivity over the range of conditions spanned by the attenuating shock. The shock pressure, density, and internal energy in quartz were determined from the observed shock velocity using the previously measured Hugoniot relation [13]. This relation was found to be almost identical to that predicted by the Kerley EOS model [14]. In fused silica, since there are no available experimental data above 100 GPa, the Kerley EOS was used. Since the difference in initial density between the fused silica and quartz Hugoniots is small, the offset between the two can be reliably predicted.

The measured shock temperatures in quartz and fused silica as a function of pressure are shown in Fig. 1. The different initial densities of these two polymorphs of silica allow the shock Hugoniots to track different paths through the silica phase diagram. The compressed densities in these experiments range between 5.2 and 7.2 g/cm³ for quartz and 4.6 to 6.2 g/cm³ for fused silica - roughly 2 to 3 times solid density. Errors in the temperature are 7-8 % near 5000 K and 4-5 % at 5×10^4 K and include systematic errors in the calibration (2-5

%), random errors due to noise on a given shot (2-3 %), and reproducibility errors derived from the variation between shots repeated under similar conditions (3-7 %). The optical reflectivity of the shock at 532 nm, defined as the fraction of energy reflected by the moving shock front, is shown in Fig. 2, with the dominant uncertainties given by reproducibility errors. The reflectivity, related to the electronic conductivity, is shown in these plots to be primarily temperature dependent.

The lowest temperatures accessed in this study are comparable to those achieved in previous gas gun experiments on both quartz and fused silica [12]. These earlier measurements observed a drop in temperature to just below 5000 K that was interpreted as melting from a superheated solid to the equilibrium liquid. Our measurements are in good agreement with the temperatures in the liquid between 5000 and 7000 K for both polymorphs, reproducing the temperature drop at melting.

To better understand the underlying mechanisms in the high-pressure liquid we have developed two separate, model-independent methods for determining the specific heat capacity, c_v , from the shock temperature measurements. The first, which we call the difference method, compares the difference in temperature and internal energy for states on the quartz and fused silica Hugoniot at the same density (i.e. volume). The specific heat is then given directly by its definition, $c_v = (\partial E / \partial T)_v \simeq [(E_f - E_q) / (T_f - T_q)]_v$, where E is the internal energy and T the temperature, with subscripts f and q representing fused silica and quartz respectively. The second method, which we call the slope method, determines c_v from the slope of the Hugoniot temperature. To quantify this idea consider that any infinitesimal section of the Hugoniot can be considered to be the sum of an isentropic compression step and an isochoric heating step such that, $\Delta E_H = \Delta E_s + \Delta E_v$ and $\Delta T_H = \Delta T_s + \Delta T_v$ where subscript v identifies a change along an isochore, s is along an isentrope, and H is along the Hugoniot. Then, using the thermodynamic definitions $(\partial E / \partial v)_s = -P$, and $\Gamma = -(v/T)(\partial T / \partial v)_s$, where P is the pressure and Γ is the Grüneisen parameter, the specific heat is given by: $c_v = \frac{\Delta E_H - \Delta E_s}{\Delta T_H - \Delta T_s} = \frac{(\partial E / \partial v)_H + P}{(\partial T / \partial v)_H + \Gamma T / v}$. The quantities on the right apart from Γ are measured directly or inferred from the known Hugoniot relation [13]. A previous study [13] found that $\Gamma \simeq 0.6$ above melting over the pressure range explored here, consistent with predictions from EOS models [14, 16]. Importantly though, c_v is quite insensitive to the value of Γ . This is because Γ is a measure of the temperature rise along an isentrope which, in strong shock waves, is a small fraction of the temperature rise along the Hugoniot. Measurements of c_v using the slope method extend over a wider range than those from the difference method, which is restricted to the subset of overlapping densities from the two Hugoniots. We use the scatter between the different

c_v measurements to determine the error in the averaged c_v .

Results from the three c_v measurements are plotted versus temperature in Fig. 3. That they all give similar results indicates that c_v is not sensitive to density. Here $\tilde{c}_v = c_v / Nk_B$ is the non-dimensional specific heat, where N is the number of atoms per unit mass and k_B is Boltzmann's constant. Previous studies in shocked silica [12] observed \tilde{c}_v to rise steeply from 3 (Dulong-Petit) once melting occurred. Our data, which extend to much higher temperatures, similarly indicate a rapid rise above melting and show the presence of a broad peak between 5000 and $\sim 35,000$ K.

In order to understand the origin of this peak we compare the data with predictions from two equation-of-state (EOS) models: one which includes molecular binding energy and the other which does not. These predictions are shown in Fig. 1 and Fig. 3. Although neither exhibit perfect agreement with our results they do generally bracket our temperature data. The quotidian EOS (qEOS) [15, 16] is a simple, phenomenological EOS model which treats the fluid by interpolation between the solid and plasma phases and does not account for the energetics of chemical bonds. The Kerley EOS [14, 17] is a liquid perturbation model that uses a chemical equilibrium approach to explicitly treat the dissociation of SiO_2 into atomic Si and O. While both models predict nearly identical Hugoniot pressures and densities, in agreement with recent experiments [13], they exhibit quite different temperature behavior and dramatically different specific heat behavior. In particular, the inclusion of bond energy in the Kerley EOS causes a sharp peak to appear in c_v between $1-2.5 \times 10^4$ K as shown in Fig. 3. This feature is absent from the bonding-free qEOS predictions and is directly attributable to the energy required to break chemical bonds. At temperatures above this peak, where bond-breaking is essentially complete, both models similarly predict that electron ionization causes a slow, monotonic rise in c_v . Much higher temperatures are required for ionization to generate peaks in c_v , a consequence of the fact that there are many fewer states available to a free electron than to a free atom. Further theoretical confirmation of this bond-breaking interpretation is given by recent quantum molecular dynamics (QMD) simulations of shocked quartz [18]. Here the calculated Si-O pair correlation function in the liquid at 7700 K exhibits a sharp peak at 1.6 - 1.7 Å, a distance corresponding to the Si-O bond length in various solid phases of silica [19]; by 38700 K this peak has mostly disappeared. This confirms that the broad peak in specific heat observed in our experiments arises from the changing short-range structure, or simply the energetics of bond-breaking. We thus define the state in the temperature range $0.5 - 3.5 \times 10^4$ K as a 'bonded liquid' (see Fig. 1) by which we mean a liquid containing a mixture of variously-sized polymerized structural units. The state of matter at higher tem-

peratures, largely devoid of chemical bonds, we term an atomic fluid.

We now estimate the change in energy and entropy of the bonded liquid caused by structural changes alone. To do this we first subtract the ionic and electronic components of c_v as approximated from the specific heat outside the bonded liquid regime [20]. The remainder, shown by the shaded region in Fig. 3, is the requisite configurational specific heat, c_v^{cfg} . Assuming that c_v^{cfg} does not change much with density along the Hugoniot (which is reasonable since the total specific heat is quite insensitive to density) we can integrate with respect to temperature between $0.5 - 3.5 \times 10^4$ K. The change in configurational energy is found to be 790 ± 50 kJ/mole (8.2 ± 0.6 eV per SiO_2 unit). This corresponds to the difference in binding energy between the liquid near melting, bound primarily by chemical bonds, and the highly-conducting atomic fluid (or dense plasma), bound by non-directional Coulomb forces. It is much greater than the latent energy of fusion (~ 150 kJ/mole) [12] but less than the cohesive energy of quartz (1859 kJ/mole). The change in configurational entropy, ΔS^{cfg} is 53 ± 5 J/mole.K. This increase in liquid configurational disorder is often used to explain the super-Arrhenius behavior of viscosity in fragile liquids via the Adam-Gibbs relation which relates kinetics to the entropy of molecular packing [21]. Such a high ΔS^{cfg} thus suggests fragile behavior in liquid silica at high temperature and pressure in contrast to its strong behavior at low pressure.

The dramatic change in transport properties associated with this onset of liquid structural disorder is exhibited by a rapid rise in electrical conductivity, as deduced from the measured shock reflectivities shown in Fig. 2. Reflectivities of more than a few percent at the shocked-unshocked interface indicate the presence of substantial electronic conductivity [22, 23]. We can roughly estimate this conductivity from the reflectivity by assuming a Drude, or free-electron type model with a minimum scattering length given by the average interatomic distance. The inferred DC conductivity, σ_0 , is shown in Fig. 4 and compared to recent QMD simulations [18] and previous shock data [24]. It is apparent that the Drude assumption overestimates σ_0 at the lowest temperatures ($T < 10^4$ K) but agrees with QMD simulations elsewhere, indicating free-electron-type behavior at high T . Inferred conductivities rise from $\sim 10^5$ S/m at 10^4 K to 5×10^5 S/m near 5×10^4 K. The QMD calculations show that this rise in DC conductivity is caused by filling of the original band gap by ‘impurity’ states, likely a combination of partially-filled bonding and anti-bonding oxygen p -states and silicon sp -hybrids, as bonds break and the liquid becomes more disordered.

Comparisons with previous data in the shocked solid [24] clearly demonstrate that a rapid rise in electron conductivity must occur immediately above the melt transition (as shown schematically by the purple line in

Fig. 4). Based on the Wiedemann-Franz relation, this indicates that thermal conductivities must also rise rapidly above melting, reaching 24-600 W/m.K between 10^4 K and 5×10^4 K. This initial rapid increase near melting combined with the slower increase at higher temperature mirrors the super-Arrhenius change in viscosity of typical fragile liquids [21]. This suggests that electron mobility in liquid silicates, like viscosity, is strongly influenced by the configurational entropy of the system.

The dissociation and enhanced electron mobility in high temperature liquid silicates have major implications for the structural, chemical, and thermal evolution of the earth after a giant planetary impact where temperatures were significantly higher than those of the present day. The lunar-forming collision, for example, is expected to have caused complete melting, generating temperatures of 10,000 K and higher throughout the silicate earth [2]. Under these conditions silicates became chemically reactive, conducting liquids providing a channel for enhanced heat and magnetic field transport across the core mantle boundary.

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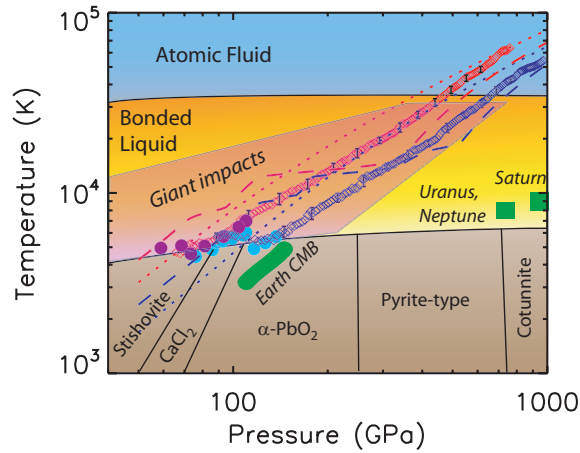


FIG. 1: Proposed phase diagram for liquid silica illustrating the bonded liquid regime, where chemical bonds dominate, and the highly-conducting atomic fluid regime, where they do not. Several known and proposed [25] solid phases are also illustrated. Shock temperatures determined in this study (densely packed diamond symbols) are given along with predictions from two EOS models: Kerley [14] (dashed lines) and qEOS [16] (dotted lines), where blue identifies quartz and red identifies fused silica. Also shown are shock data from Lyzenga and Ahrens [12] (purple dots for fused silica, light blue for quartz).

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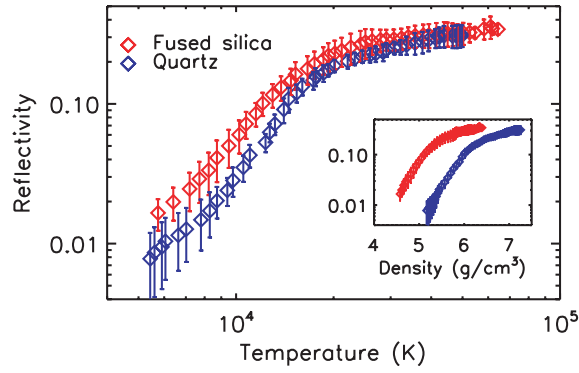


FIG. 2: Shock reflectivity in quartz (blue) and fused silica (red) shown as a function of temperature and density. The data indicate a primarily temperature-driven mechanism relatively insensitive to density.

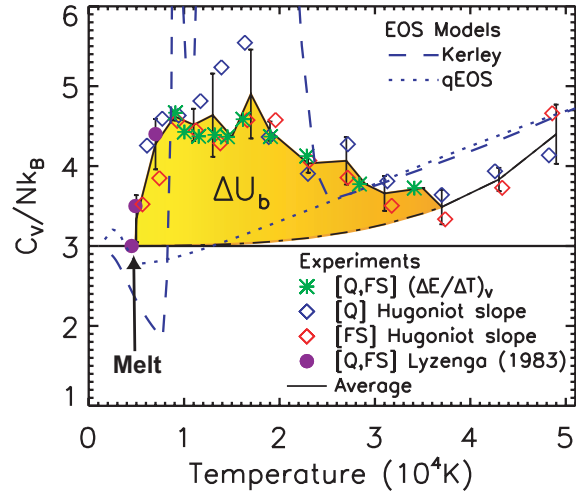


FIG. 3: The specific heat as determined by the difference method (green asterisks), the slope of the quartz Hugoniot (blue diamonds), and the slope of the fused silica Hugoniot (red diamonds). The Dulong-Petit limit is 3 in these normalized units. Purple dots show previous data [12]. The black line gives the average of all these results (current data and previous data). The Kerley [14] model which includes bonding effects shows a peak in c_v after melting; the qEOS model [16] which ignores chemical bonds does not. The shaded area we define as the excess, or configurational specific heat [20].

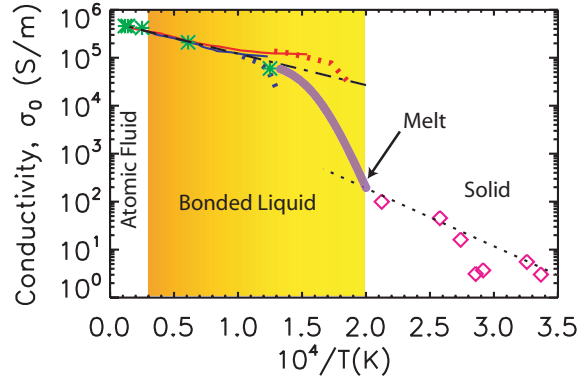


FIG. 4: The inferred conductivity versus the reciprocal temperature for quartz (blue line) and fused silica (red line) is almost identical to QMD predictions [18] above 10^4 K (green asterisks). A fit to the form, $\sigma_0 = \sigma_{00}\exp(-E_a/k_B T)$ gives $\sigma_{00} = 5.5 \times 10^5$ S/m and $E_a = 1.3$ eV and is shown by the dot-dashed line. Below 10^4 K the Drude model fails because it assumes a positive value for the imaginary part of the conductivity, σ_2 ; dotted lines show the result if σ_2 is set to zero. Previous shock data [24] (pink diamonds) and the corresponding fit (dotted line) are also shown. The combined data suggest a sudden jump in conductivity upon melting (purple line).